

Importance of bond exchange in MnC structural stability and half-metallic ferromagnetism: A comprehensive benchmark density functional study

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Recently, the first successful synthesis of bulk manganese monocarbide (MnC) has been reported. The compound crystallizes in the zinc-blende structure and has been proposed as a potential superhard material. In this work, we present a comprehensive first-principles study of the structural, electronic, and magnetic properties of MnC using several exchange-correlation approximations. We demonstrate that the SCAN meta-GGA (generalized gradient approximation) and the Perdew-Burke-Ernzerhof zero revised (PBE0r) hybrid functional outperform GGA-Perdew-Burke-Ernzerhof for solids (PBEsol), Heyd-Scuseria-Ernzerhof 2006 (HSE06), and the mean-field density functional theory [(DFT)] + U + V schemes in correctly predicting the experimentally observed zinc-blende structure as the ground state. Our analysis reveals that the bond-exchange interaction plays a decisive role in stabilizing this phase. At theoretical equilibrium, hybrid functionals (PBE0r and HSE06) predict a metallic ground state, whereas semilocal functionals (PBEsol and SCAN) and DFT + U + V yield two distinct types of half-metallic ferromagnetism with opposite volume dependence, opening a debate on the origin and nature of this behavior. If confirmed experimentally, such a property would make MnC an attractive candidate for spintronic applications.

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I. INTRODUCTION

The stoichiometric binary monocompounds arising from late 3d transition metal (Mn, Fe, Co, Ni, and Cu) and light elements (C, N, and O) show a variety of interesting physical properties. Among them, the monoxides (e.g., MnO, FeO, and NiO), have been well known for a long time and their properties are well established experimentally and theoretically [1–3]. These systems, which crystallize in the rocksalt structure, have served for decades as benchmark materials for the study of strong correlations [4,5].

In contrast, the corresponding mononitrides remained more challenging experimentally until the end of the past century [6–9]. For instance, the experimentally observed antiferromagnetic MnN, in a distorted rocksalt structure, is currently well established [10,11]. On the other side, the crystal structure FeN and CoN was the subject of some debate [12,13], but it was confirmed later that both adopt a zinc-blende one [14]. Finally, NiN and CuN remain experimentally unknown, and some *ab initio* predictions of their ground-state structure continue to disagree [15–17].

The situation is more complicated for monocarbides (MnC, FeC, etc.), which are hardly known. Their difficult synthesis is mainly attributed to the progressive filling of the antibonding

states along the late 3d series, which weakens the metal-carbon bonding and makes the stoichiometric phases highly unstable [18–20]. Nevertheless, some *ab initio* investigations have addressed their structural and thermodynamic stability in the rocksalt phase [21,22]. It has been concluded that MnC and FeC are unstable at ambient conditions, but could be stabilized under high pressure or temperature. Interestingly, an unconventional superconductivity was also predicted in MnC [22]. A similar study has demonstrated that MnC would be more stable in hexagonal wurtzite structure [23].

According to the calculated formation enthalpies of the manganese-carbon system, the stoichiometric MnC formation is highly unfavorable [24]. Recently, however, a first successful synthesis was achieved under high-pressure and high-temperature conditions [25]. The compound was found to be a metal adopting the fourfold-coordinated zinc-blende (ZB) structure, with a lattice constant of 4.429 Å, and suggested as a potential superhard material. However, no data have been provided about its magnetic properties. This experimental achievement presents a theoretical puzzle, since recent calculations concluded that under pressure, MnC would be stable in the rocksalt structure [22]. Moreover, early theoretical investigations predicted zinc-blende MnC as half-metallic ferromagnet with an unusual coexistence of localized and itinerant magnetic moments [26–28]. This property (e.g., full spin polarization at Fermi level) is highly desirable for spintronic applications [29,30].

This raises a fundamental question about the accurate first-principles framework to simultaneously describe the structural stability, electronic, and magnetic properties of MnC. The answer is nontrivial, as it requires a method capable to capture correctly the interplay between covalent

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Mn–C bonding, electronic correlations, and exchange interactions.

Motivated by these developments, we present a comprehensive density functional theory (DFT) study of MnC. We employ a hierarchy of exchange-correlation functionals, ranging from semilocal generalized gradient approximation (GGA) and meta-GGA to range-separated hybrids and the extended DFT + U + V approach, with a specific focus on the role of *bond-exchange* interactions. Our goals are threefold: to identify the functional that correctly stabilizes the observed ZB phase, to uncover the physical mechanism behind this stabilization, and to resolve the conflicting predictions regarding its electronic behavior.

The paper is organized as follows: Section II outlines the theoretical methods, where the basics of meta-GGA, hybrid DFT functionals, and the extended DFT + U + V approach are presented. The computational details are given in Sec. III. The structural stability and the magnetic ordering are discussed in Sec. IV, and we analyze the electronic structure and chemical bonding in Sec. V. To conclude our investigation, we summarize the important results in Sec. VI.

II. THEORY

Although density functional theory (DFT) is, in principle, an exact ground-state theory, the exact form of the exchange-correlation energy functional E_{xc} remains unknown [31]. Therefore, the practical usage of the Kohn-Sham framework [32] relies entirely on finding suitable approximations, and a panoply of schemes and parametrizations have been developed over time. The classification of the main theoretical advances is nicely illustrated by the Perdew Jacob's ladder [33], which ranks functionals by their degree of nonlocality.

A. Semilocal functionals

1. GGA

In the second rung of Jacob's ladder, one can find the generalized gradient approximation (GGA) exchange-correlation energy functionals. One of the most widespread GGA is the Perdew, Burke, Ernzerhof (PBE) functional [34]. A newer variant, having the same functional form, is the PBE for solids (commonly known as PBEsol) [35]. While PBE works well in chemistry (often accurate for molecules with high-density gradients), PBEsol is a reparametrization that aims to improve the study of solids where density gradients are lower. It is especially designed to give a better description of solid-state systems properties (like lattice constants and bulk moduli).

2. Meta-GGA

The so-called meta-generalized gradient approximations (meta-GGAs) constitute the highest semilocal rung of Jacob's ladder hierarchy avoiding the full nonlocality. Like GGAs, they depend on the electron density $n_\sigma(\mathbf{r})$ and its gradient $\nabla n_\sigma(\mathbf{r})$, but they additionally incorporate the positive kinetic-energy density $\tau_\sigma(\mathbf{r})$ ¹, where $\sigma = \{\uparrow, \downarrow\}$ is the spin index

[33]:

$$E_{xc}^{\text{MTGGA}}[n_\sigma] = \int d\mathbf{r} \varepsilon_{xc}^{\text{MTGGA}}(n_\sigma, \nabla n_\sigma, \tau_\sigma). \quad (1)$$

The kinetic-energy densities are constructed from the Kohn-Sham orbitals:

$$\tau_\sigma(\mathbf{r}) = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \phi_i^\sigma(\mathbf{r})|^2. \quad (2)$$

Several parametrizations of the meta-GGA exist in literature, where the well known are the Tao-Perdew-Staroverov-Scuseria (TPSS) [37], its revised version rev-TPPS [38], Minnesota 2006 Local (M06L) [39], and modified Becke-Johnson (mBJ) [40]. The recently proposed one, namely the strongly constrained and appropriately normed (SCAN) functional [41], has attracted much attention. According to the authors, the most important ingredient making the SCAN superior to previous meta-GGAs is the dimensionless parameter of the kinetic-energy densities:

$$\alpha = \frac{\tau_\sigma(\mathbf{r}) - \tau_\sigma^{\text{W}}(\mathbf{r})}{\tau_\sigma^{\text{unif}}(\mathbf{r})}, \quad (3)$$

where $\tau_\sigma^{\text{W}}(\mathbf{r})$ represents the single-orbital limit of $\tau_\sigma(\mathbf{r})$, and $\tau_\sigma^{\text{unif}}(\mathbf{r})$ is the uniform-density limit.

The variable α distinguishes three different bonding characters: covalent ($\alpha = 0$), metallic ($\alpha = 1$), and weak ($\alpha \gg 1$). Many SCAN calculations, on diverse molecular and extended systems, have demonstrated that it leads to very interesting results, especially for structural geometry and energetics [42–46]. Moreover, it is argued that the SCAN functional could be suitable (at least qualitatively) for the treatment of strong electronic correlations [47,48], and the related ground-state symmetry breaking [49]. We notice finally that two revised formulation of the SCAN functional, known as rSCAN [50] and r2SCAN [51], have been recently proposed.

B. Hybrid functionals

An outstanding improvement, beyond semilocal DFT, is the *hybrid* (Hartree-Fock±DFT) functionals. The basic idea, initially proposed by Becke [52,53], is to incorporate a fraction of nonlocal exact exchange from Hartree-Fock (HF) theory into the semilocal E_{xc} . He suggested a simple linear combination:

$$E_{xc}^{\text{hybrid}} = E_{xc}^{\text{GGA}} + \beta(E_x^{\text{HF}} - E_x^{\text{GGA}}), \quad (4)$$

where β is obtained by some fitting to the atomization energies. A later improved version, the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) functional [54], has become very popular in the quantum chemistry community. A next step is the PBE0, described as a parameter-free functional [55]. Based on GGA-PBE [34], it is derived from Eq. (4) with a predefined fraction ($\beta = \frac{1}{4}$), justified by a general analysis from perturbation theory [56]:

$$E_{xc}^{\text{PBE0}} = E_{xc}^{\text{PBE}} + \frac{1}{4}(E_x^{\text{HF}} - E_x^{\text{PBE}}). \quad (5)$$

While the previous functionals belong to the family of *global* hybrid functionals, an important advance is the so-called *range-separated* hybrid functionals, using a *screened*

¹Notice that in addition, the Laplacians of the electron densities $\nabla^2 n_\sigma(\mathbf{r})$, can be incorporated into the meta-GGA functionals [36].

interaction instead of the bare Coulomb potential [57,58]. In extended systems, this idea is very appealing not only technically but also physically. A screened interaction makes the HF exchange more tractable, and accounts for the screening phenomenon established by the random-phase approximation [59,60].

In HSE hybrid functionals [57,58], the separation (and the screening as a result) is achieved by an error function decomposing the bare Coulomb potential into a short-range (SR) and a long-range (LR) part:

$$\frac{1}{r} = \underbrace{\frac{1 - \text{erf}(\omega r)}{r}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{\text{LR}}, \quad (6)$$

where ω is an adjustable screening parameter (with a value of $\omega=0.11 \text{ bohr}^{-1}$ recommended for solids [61]). The HSE exchange-correlation functional is expressed as

$$E_{\text{xc}}^{\text{HSE}} = \frac{1}{4}E_{\text{x}}^{\text{HF-SR}} + \frac{3}{4}E_{\text{x}}^{\text{PBE-SR}} + E_{\text{x}}^{\text{PBE-LR}} + E_{\text{c}}^{\text{PBE}}. \quad (7)$$

In fact, GGA-PBE and PBE0 hybrid functional are merely restored, from the two particular values $\omega = \infty$ and $\omega = 0$, respectively. In Eq. (7), only the first term needs to be calculated exactly, and all the remaining ones are computed at the PBE level. Even with this simplification, the HF exact exchange is computationally very expensive. With the Kohn-Sham orbitals $\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$, with n the electronic band index and $\mathbf{k}$ the Bloch wave vector, it is defined as

$$E_{\text{x}}^{\text{HF-SR}} = -\frac{1}{2} \sum_{\sigma} \sum_{n,\mathbf{k}} \sum_{n',\mathbf{k}'} \int d^3r \int d^3r' (1 - \text{erf}(\omega|\mathbf{r} - \mathbf{r}'|)) \times \frac{e^2 \phi_{n,\mathbf{k}}^{\sigma*}(\mathbf{r}) \phi_{n',\mathbf{k}'}^{\sigma}(\mathbf{r}) \phi_{n',\mathbf{k}'}^{\sigma*}(\mathbf{r}') \phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}. \quad (8)$$

C. Orbital-selective hybrid functional

More progress in this field is the recently invented *orbital-selective* hybrid functional and so-called PBE0r [62]. The Kohn-Sham orbitals $\phi_{n,\mathbf{k}}^{\sigma}(\mathbf{r})$ are expanded in a minimal basis of localized atom-centered tight-binding orbitals $\chi_{\alpha}^{\sigma}(\mathbf{r})$. The latter are constructed from a combination of numerical solutions of the Schrödinger equation for the isolated atom in the inner region, and Hankel functions as tails in the outer region. Here, the HF exact exchange energy is expressed as

$$E_{\text{x}}^{\text{HF}} = -\frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \sum_{\sigma,\sigma'} \rho_{\delta,\alpha} \rho_{\gamma,\beta} \int d^3r \int d^3r' \times \frac{e^2 \chi_{\alpha}^{\sigma*}(\mathbf{r}) \chi_{\beta}^{\sigma'}(\mathbf{r}') \chi_{\gamma}^{\sigma}(\mathbf{r}) \chi_{\delta}^{\sigma'}(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}, \quad (9)$$

where the density matrix elements $\rho_{\delta,\alpha}$ are defined as²

$$\rho_{\delta,\alpha} = \sum_{\sigma} \sum_{n,\mathbf{k}} \langle \chi_{\delta} | \phi_{n,\mathbf{k}}^{\sigma} \rangle f_{n,\mathbf{k}}^{\sigma} \langle \phi_{n,\mathbf{k}}^{\sigma} | \chi_{\alpha} \rangle. \quad (10)$$

²In a general noncollinear formulation, the Kohn-Sham states should be two-component Pauli spinor wave functions. Here in Eq. (10), however, we follow the same notation that is used in the papers we refer to, describing only the collinear case.

and $f_{n,\mathbf{k}}^{\sigma}$ are the occupations of the Kohn-Sham states. The second line in Eq. (9) represents the Coulomb matrix elements in local orbitals, called the four-center integrals. This approach allows a natural decomposition of the HF exchange into the following:

(1) *On-site* exchange acting between states centered on the same atom. It affects the degenerate states and split them into filled and empty bands (the Mott-Hubbard separation in the narrow- and partially filled d - and f atomic shells).

(2) *Bond -exchange* describing the intersite exchange between electron densities located at neighboring atoms involved in chemical bonds.

(3) *Long-range* exchange acting over distances longer than bond lengths. The neglect of this term is indeed advantageous, since the unphysical behavior in metallic solids (due to the long-range tail of the Coulomb interaction) is avoided and the screening is effectively taken into account.

The bond-exchange term is particularly relevant for covalently bonded materials, as it differentiates between bonding and antibonding states. It mainly corrects the semilocal functional errors in formation energy and band gaps. Notice that this type of exchange is different from conventional on-site exchange, and should not also be confused with other magnetic-ordering-related mechanisms (like double exchange, or superexchange).

The use of localized atom-centered orbitals (a natural cutoff of the exchange interaction) and the neglect of the long-range exchange terms (capturing the important screening effects) make PBE0r a *de facto* screened hybrid functional.

The exchange-correlation energy functional $E_{\text{xc}}^{\text{PBE0r}}$ is defined as follows:

$$E_{\text{xc}}^{\text{PBE0r}} = E_{\text{xc}}^{\text{PBE}} + \sum_{\mathbf{R}} a_{\mathbf{R}} (E_{\text{x},\mathbf{R}}^{\text{HF-on-site}} - E_{\text{x},\mathbf{R}}^{\text{PBE-on-site}}) + \frac{1}{2} \sum_{\mathbf{R}} \sum_{\mathbf{R}' \neq \mathbf{R}} \frac{a_{\mathbf{R}} + a_{\mathbf{R}'}}{2} (E_{\text{x},(\mathbf{R},\mathbf{R}')}^{\text{HF-intersite}} - E_{\text{x},(\mathbf{R},\mathbf{R}')}^{\text{PBE-intersite}}). \quad (11)$$

(1) The first sum runs over the atoms in the unit cell. Each term involves four orbitals centered on the same site. The mixing factor $a_{\mathbf{R}}$ represents the local screening. Here, $E_{\text{x},\mathbf{R}}^{\text{HF-on-site}}$ and $E_{\text{x},\mathbf{R}}^{\text{PBE-on-site}}$ represent the exchange energies calculated on the same site. While the former is calculated using the exact exchange (Hartree-Fock), the latter is evaluated with the local exchange of the GGA-PBE and then subtracted to avoid double counting.

(2) In the second double sum, the first index runs over the atoms in the unit cell, while the second index runs over all neighbors within a specified radius. This term accounts for the bond exchange. Each term involves the product of two density matrices connecting orbitals from the neighboring sites, and the Coulomb interaction between densities on either side.

This formulation of PBE0r is very flexible, since the mixing factor $a_{\mathbf{R}}$ can be set differently for the atomic species, and allows an explicit control of the bond-exchange contribution.

Finally, the accuracy of PBE0r versus experiments has been established for a large variety of systems, such as partially filled d -shell oxides [63], transition-metal sulfides and

nitrides [29,64,65], manganese oxides [66], ultrawide band-gap dioxide [67], and iron spin-crossover complexes [68].

D. Hubbard-corrected DFT

In this section, we summarize the basic notions of the Hubbard-corrected DFT methods. We concentrate on the recently proposed DFT + U + V formalism [69] (based on the extended Hubbard model), from which the widely used DFT + U [70–72] can be straightforwardly derived. Starting from any local or semilocal functional, the corresponding DFT + U + V one is written as

$$E_{xc}^{\text{DFT}+U+V} = E_{xc}^{\text{DFT}} + E_{xc}^{U+V}. \quad (12)$$

Following the definition and the notation adopted in Refs. [69,73], the Hubbard correction to the exchange-correlation energy (in the simplified rotationally invariant formulation) is given by

$$E_{xc}^{U+V} = \frac{1}{2} \sum_I \sum_{\sigma mm'} U^I (\delta_{mm'} - n_{mm'}^{II\sigma}) n_{m'm}^{II\sigma} - \frac{1}{2} \sum_I \sum_{J \neq I} \sum_{\sigma mm'} V^{IJ} n_{mm'}^{IJ\sigma} n_{m'm}^{JI\sigma}, \quad (13)$$

where U^I and V^{IJ} are, respectively, the on-site and the intersite Hubbard parameters. Notice that the double-counting corrections E_{dc} , for on-site and intersite terms, are implicitly included, i.e., $E_{xc}^{U+V} = E_{\text{Hub}} - E_{dc}$ (It is the term connected to the Kronecker delta, appearing explicitly in Eq. (4) and Eq. (12) of the original work by Campo and Cococcioni [69]). The index I runs over all the atomic sites, typically transition metal, for which the on-site correction is applied to their d -shell orbitals. In the second line, the sum over J covers all neighboring atoms up to a given distance (typically the ligand nearest neighbors).

In Eq. (13), the occupation matrix elements $n_{mm'}^{IJ\sigma}$ are obtained by the projection of the Kohn-Sham states $|\phi_{n,\mathbf{k}}^\sigma\rangle$ on a set of orthogonalized atomic orbitals $|\chi_m^I\rangle$:

$$n_{mm'}^{IJ\sigma} = \sum_{n,\mathbf{k}} \langle \chi_m^I | \phi_{n,\mathbf{k}}^\sigma \rangle f_{n,\mathbf{k}}^\sigma \langle \phi_{n,\mathbf{k}}^\sigma | \chi_{m'}^J \rangle, \quad (14)$$

where $f_{n,\mathbf{k}}^\sigma$ represent again the occupations of the Kohn-Sham states. The m (m') index is the magnetic quantum number, running over the orbital momentum in atom I (J). Notice that the on-site occupation elements $n_{mm'}^{II\sigma}$ can be obtained as a particular case ($I = J$).

At this point, it is important to mention the issue about the values of U and V parameters. These latter are actually unknown, and they are usually tuned by hand to reproduce some experimental data (like lattice constants, magnetic moments, and more importantly, band gaps). Such a procedure, however, makes DFT + U + V a partially empirical method. In fact, there exist several first-principles techniques to compute the correct values of U and V . Some of those well known are the constrained DFT (cDFT) [74–76] and the constrained random-phase approximation [77–79]. A recent one, using density functional perturbation theory (DFPT) [80,81], has been developed with the main advantage of a significant reduction in the computational cost.

Last but not least, these Hubbard parameters depend intimately on the chemical environment from which they are computed. Thus, they are not transferables, i.e., not universal for a given atomic species [82]. In addition, they depend on the kind of the projector functions used [83,84].

III. COMPUTATIONAL DETAILS

All calculations were performed within DFT [31,32], using three different exchange-correlation schemes: the semilocal framework (GGA-PBESol [35] and SCAN meta-GGA [41]), two range-separated hybrid functionals (HSE06 [58] and PBE0r [62]), and the mean-field DFT + U + V approach [69]. In the latter, the double-counting correction is accounted using the *fully localized limit* formulation [71,85–87].

The PBESol, SCAN, HSE06, and DFT + U + V calculations were carried out using the QUANTUM ESPRESSO package (qe, version 7.1) [88–90]. In the PBESol, HSE06, and DFT + U + V , the Kohn-Sham single-particle equations were solved within the projector-augmented wave (PAW) method [91], using PAW potentials from the PSLibrary [92]. For SCAN meta-GGA, however, norm-conserving pseudopotentials from the PseudoDojo library [93] were employed. The screening parameter ω in HSE06 was set to 0.11 bohr⁻¹, which is the recommended value for solid systems [61].

Based on density functional perturbation theory (DFPT), within the linear-response formalism, the on-site U and intersite V parameters were calculated self-consistently using the HP code [94] (distributed within the qe package). The Γ -centered $\mathbf{q}$ -point mesh was increased up to $3 \times 3 \times 3$ to ensure convergence. Orthogonalized atomic orbitals, obtained via the Löwdin method [83,94,95], were used as Hubbard projector functions. Since U and V are not transferables, they were computed separately for the rocksalt and zinc-blende structures, at each step of the total energy versus volume optimization.

All calculations were converged with a plane-wave kinetic-energy cutoff of 50 Ry, with a total-energy threshold of 10^{-8} Ry in the self-consistent cycle. The Brillouin zone was sampled following the Monkhorst-Pack scheme [96], using a $18 \times 18 \times 18$ mesh (200 $\mathbf{k}$ -point). For metallic states, the electronic smearing was treated using the Marzari-Vanderbilt scheme [97], with a broadening parameter of 0.02 Ry. The calculations of the electronic densities of states, however, were carried out with the improved linear tetrahedron method [98].

The PBE0r hybrid functional calculations were performed using the PAW method [91], within its original implementation provided in the CP-PAW code [99]. We recall that PAW is by construction an *all-electron* method, using augmented waves. The included orbitals in the PAW augmentation are: 2s, 2p, and 3d of C, and 3s, 3p, 3d, 4s, and 4p of Mn, with covalent radii of 0.71 Å (C) and 1.17 Å (Mn). In addition, Mn 3s and 3p semicore states were treated as valence orbitals. As mentioned above in Sec. II B, PBE0r uses a localized tight-binding orbitals basis, including the 2s and 2p orbitals of C, and the 3s, 3p, 3d, and 4s ones of Mn.

The CP-PAW code uses Car-Parrinello *ab initio* molecular dynamics (MD) [100], where the ground state is reached by applying a friction term (a damped MD). Here also, and to

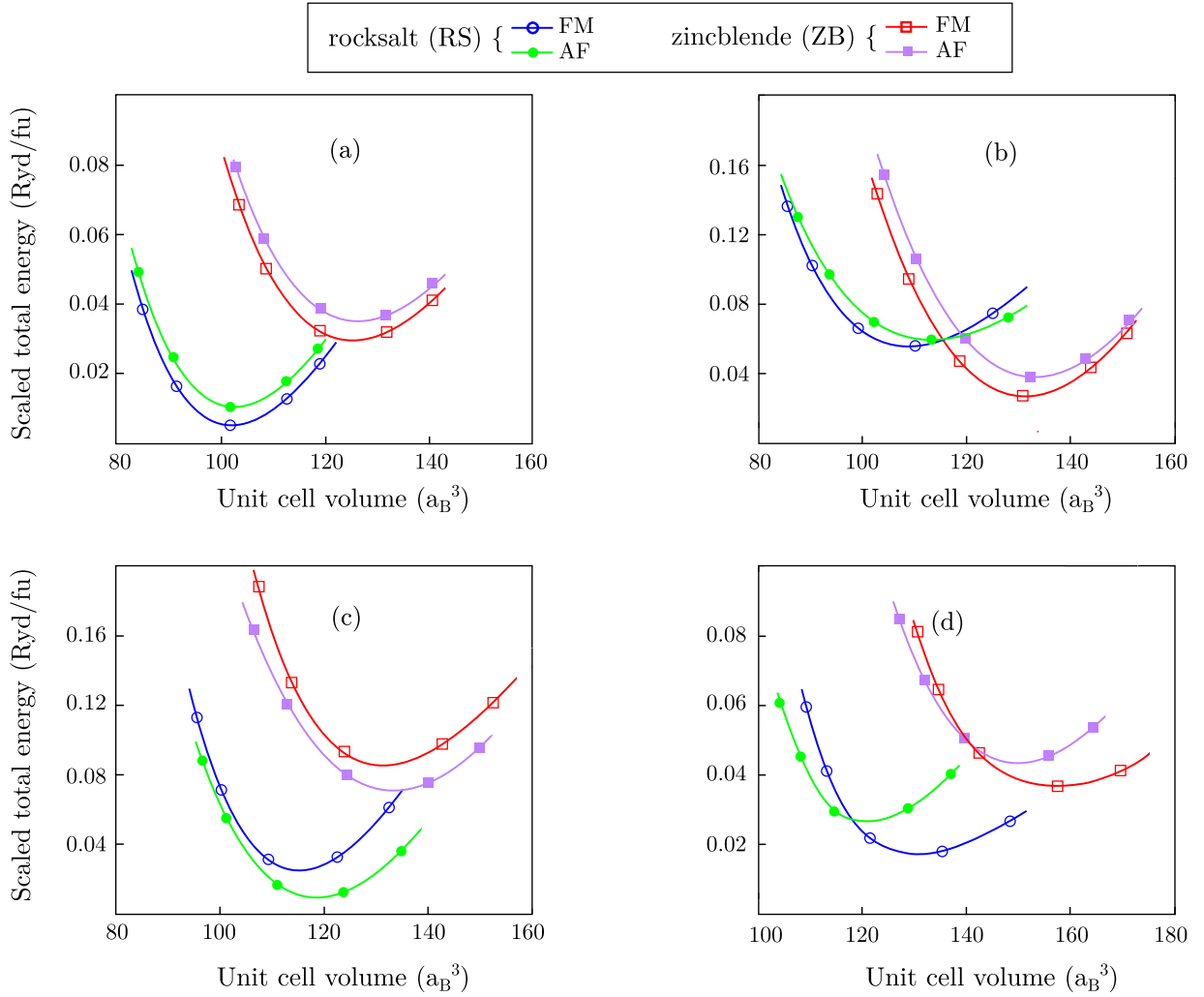


FIG. 1. Energy vs volume optimization of MnC in rocksalt (RS) and zinc-blende (ZB) structures, as obtained within qe: (a) PBEsol, (b) SCAN, (c) HSE06, and (d) DFT + U + V functionals.

be in line with qe calculations, a plane-wave kinetic-energy cutoff of 50 Ry for the auxiliary wave functions was used. The total energy was minimized up to a convergence threshold of 10^{-5} hartree, and the improved linear tetrahedron method [98] was used for the Brillouin-zone integration (with 200 $\mathbf{k}$ points). To deal with fractional occupations in metallic systems, the Mermin functional [101] was used.

A significant advantage of PBE0r functional is its low computational cost, which is comparable to GGA [66,67]. In the present study, the same value of the mixing factor is assigned for both C and Mn atoms. As mentioned above (Sec. II B), however, HSE06 calculations are extremely expensive, especially with plane waves [73]. To assess the exact exchange effect on MnC properties, we have used two fractions of the exact exchange: 10 and 30%, with a $3 \times 3 \times 3$ uniform $\mathbf{q}$ -point mesh.

IV. GROUND-STATE CRYSTAL STRUCTURE AND MAGNETIC ORDER

Structural stability of MnC is investigated in the two face-centered-cubic: rocksalt (RS) and zinc-blende (ZB) structures.

This choice is motivated by the fact that all known monoxides, mononitrides, and monocarbides are found to crystallize in either of these two prototypes. For each structure, both spin-polarized ferromagnetic (FM) and type-II antiferromagnetic (AF-II) are considered. In the latter, ferromagnetic planes alternate along the $\langle 111 \rangle$ direction, as commonly observed in MnO and NiO.

As a side note, additional calculations for MnC in the wurtzite structure were performed. It was found to be the most unstable phase and the corresponding results are therefore omitted.

A. Structural stability

Theoretical ground state is obtained from the energy versus volume optimization. The results from PBEsol, SCAN, HSE06, and DFT + U + V are shown in Fig. 1, and those from PBE0r (with and without the inclusion of bond exchange) are presented in Fig. 2. The curves were fitted with the third-order of the Birch-Murnaghan equation of state [102]. The important finding is that SCAN and PBE0r successfully reproduce the experimentally observed zinc-blende

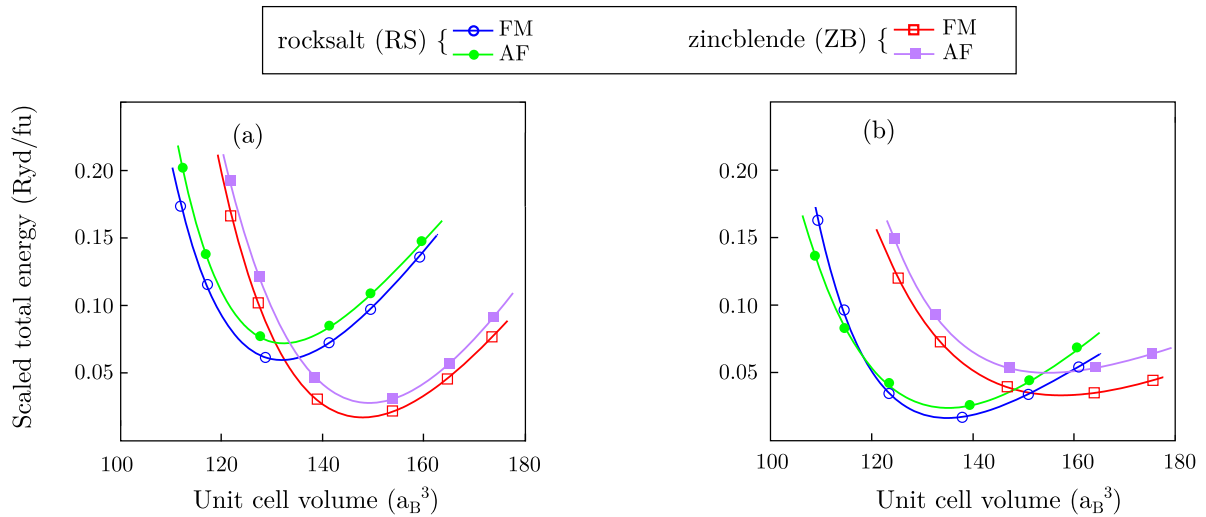


FIG. 2. Energy vs volume optimization of MnC in RS and ZB structures, as obtained within the PBE0r functional: (a) PBE0r (offsite= T) with the bond exchange, and (b) PBE0r (offsite= F) without the bond exchange.

ground-state structure, while the others incorrectly stabilize the rocksalt one. The computed total-energy differences at equilibrium are provided in Table I. It is important to mention that for PBE0r, only a 10% fraction of exact exchange was sufficient to reproduce the correct structure, whereas with a fraction as high as 30%, HSE06 still predicts a stable rocksalt phase.

The failure of the GGA-type functionals is actually not new, and has been reported in several other cases, such as MnN compound [9,13,103]. In that case, however, hybrid functionals and GGA + U approaches were able to remedy this issue [11]. Interestingly, neither the usually accurate HSE06 nor the DFT + U + V method are able to predict the correct MnC structure.

B. Role of bond exchange

The structural stability of the zinc-blende phase over the rocksalt one can be addressed using the flexibility of PBE0r framework, where the results of two kinds of calculations are shown in Fig. 2:

(1) a) with bond-exchange included (offsite= T , which refers to the exchange interaction offsite terms); and

(2) b) without bond-exchange, i.e., only on-site exchange (offsite= F)

These results provide explicit evidence of the importance of the bond-exchange term in stabilizing the ZB phase. When it is ignored, the rocksalt phase becomes energetically favored. This exchange term has the characteristic to distinguish between bonding and antibonding states, and acts differently on their occupations. As a result, it accounts better for the covalency effects and reduces the formation energy errors. To assess quantitatively this contribution in each phase, the total energy difference $\Delta E = E_{\text{offsite} = T} - E_{\text{offsite} = F}$ is provided: $E \Delta_{\text{RS}} = -0.196$ Ry and $E \Delta_{\text{ZB}} = -0.311$ Ry. This shows clearly that neglecting the bond-exchange contribution introduces a much larger error in the zincblende structure than in the rocksalt one.

Concerning SCAN functional, its main advantage is the ability to recognize different types of bonding. From benchmark calculations (up to 1000 compounds known experimentally), it was found that the formation energy errors in covalent systems decrease substantially (by $\sim 50\%$ compared to GGA-PBE). The reason behind this success is the enhanced exchange interaction in the covalent regime [40,44]. This agreement between SCAN and PBE0r indicates that the enhanced exchange interaction built into SCAN plays a role analogous to the explicit bond-exchange in PBE0r.

Both frameworks highlight the important role of covalent exchange effects in MnC. In fact, the Mn-C bond involves significant hybridization between Mn- $3d$ and C- $2p$ orbitals; thus, conventional GGAs treating exchange isotropically underestimate the energy gain associated with covalent bonding. The explicit inclusion of this term (PBE0r) or its implicit treatment via the kinetic-energy density parameter (SCAN) both strengthen Mn-C hybridization. These findings emphasize that accurate treatment of bond-directional exchange is crucial for describing structural stability in late $3d$ transition-metal carbides, where the interplay between metallic and covalent bonding is not clear-cut.

We believe that the inability of HSE06 to capture this stabilization can be attributed to a subtle competition between

TABLE I. Calculated total energies differences (in Ry/f.u.) between FM and AF-II orders in the RS and (ZB) structures, and between the two phases at theoretical equilibrium, as arising from all the frameworks.

	$E_{\text{FM}} - E_{\text{AF-II}}$		
	RS	ZB	$E_{\text{RS}} - E_{\text{ZB}}$
PBEsol	-0.003	-0.005	-0.028
SCAN	-0.006	-0.008	+0.035
PBE0r	-0.015	-0.010	+0.043
HSE06	+0.020	+0.015	-0.045
DFT + U + V	-0.008	-0.005	-0.029

TABLE II. Calculated equilibrium properties within all the used frameworks, for MnC in rocksalt (RS) and zincblende (ZB) structures. The lattice constant a in Å, the magnetic moment per formula unit M_{fu} in μ_B (in the FM case), and the bulk modulus B in GPa are shown.

	a	RS B	M_{fu}	a	ZB B	M_{fu}
PBESol						
FM	3.97	230	1.15	4.22	172	1.00
AF	3.98	232		4.23	166	
SCAN						
FM	4.02	224	1.30	4.28	175	1.00
AF	4.08	219		4.31	169	
PBE0r						
FM	4.15	214	2.88	4.44	192	2.05
AF	4.17	210		4.48	150	
HSE06						
FM	4.10	238	2.58	4.32	201	1.94
AF	4.14	220		4.35	189	
DFT + U + V						
FM	4.27	211	3.04	4.51	116	3.00
AF	4.17	204		4.46	102	
Theory						
Ref. [23]	4.02	295		4.31	240	
Ref. [26]				4.23		
Ref. [28]				4.20		
Experiment						
Ref. [25]				4.43	170	

electron localization and covalent bonding and the absence of bond-selective exchange. HSE06 mixes a fixed fraction of exact exchange into the PBE functional, but still treats bonding and antibonding states on equal footing. The same argument hold as well for the DFT + U + V method, despite the existence of V intersite parameter.

C. Equilibrium properties and magnetic ordering

The equilibrium values of lattice constants (in Å), bulk moduli (in GPa), and magnetic moments per formula unit M_{fu} (in μ_B) obtained from each framework are summarized in Table II, along with available theoretical and experimental data.

Compared to the only available experimental lattice constant of zinc-blende MnC [25], semilocal PBESol and SCAN functionals tend to underestimate it, while DFT + U + V overestimates it. On the other side, the hybrid functionals yield a close agreement with experiment. In particular the PBE0r result of 4.44 Å is almost perfect. Yet, while such agreement with experiment is necessary for the reliability of any theoretical study, this should not be taken as a definitive validation of the experimental results. To our knowledge, MnC has not been elaborated in the rocksalt structure, and our PBESol results agree very well with previous GGA calculations [22,23]. The bulk moduli follow an opposite trend: semilocal functionals agree better with experimental results, whereas hybrid and DFT + U + V schemes yield stiffer or softer lattices, respectively.

Total energies differences between the FM and AF-II states, in both crystal structures are provided in Table I. The FM order is energetically favored over the AF-II configuration in all frameworks, except in HSE06 where the opposite is

predicted. The computed magnetic moments per formula unit reveal clear functional-dependent trends, with larger values in the RS phase. While PBESol and SCAN yield smaller moment, hybrid functionals (HSE06 and PBE0r) enhance the exchange splitting and produce larger values. Finally, the DFT + U + V method yields the largest moments, reflecting stronger on-site exchange interactions.

The integer magnetic moments obtained within semilocal and DFT + U + V frameworks suggest a half-metallic nature for ZB-MnC. This prediction is examined in more detail in the following section.

V. ELECTRONIC STRUCTURE AND BONDING PROPERTIES

In this section, we analyze the electronic structure and chemical bonding properties of MnC in both rocksalt (RS) and zincblende (ZB) phases. The results are presented in terms of the site-, orbital-, and spin-projected densities of states (PDOS), as computed within the various exchange–correlation frameworks discussed above. To elucidate the crystal-field effects, the Mn-3d states are split into Mn- t_{2g} and Mn- e_g manifolds, corresponding to octahedral and tetrahedral coordination, respectively. In addition, we concentrate on the ground-state spin-polarized ferromagnetic configuration, where particular attention is paid to the nature of half-metallic ferromagnetism and to how the choice of functional affects the Mn–C bonding and spin polarization.

A. Semilocal PBESol and SCAN

First, the MnC electronic structure is explored within the PBESol functional, where the obtained densities of states are

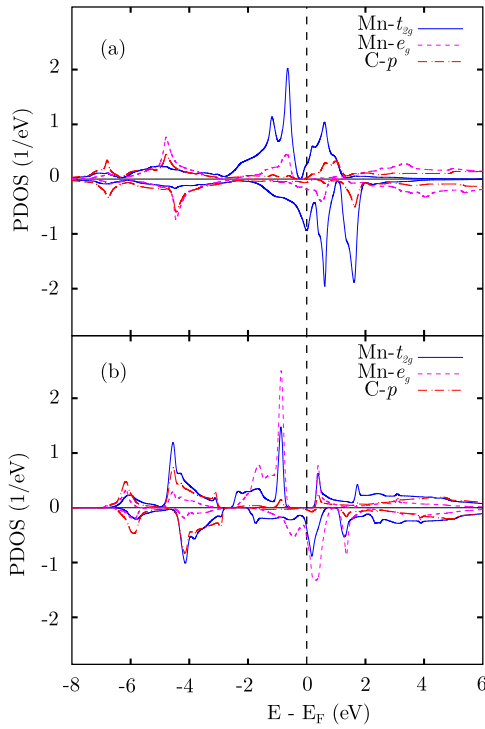


FIG. 3. Atom- and spin-resolved densities of states (PDOS) of MnC in RS-type (a) and ZB-type (b) structures, as arising from the PBEsol spin-polarized FM calculations.

shown in Fig. 3. In general, there are three main regions corresponding to bonding, nonbonding, and antibonding states.

For the rocksalt structure (the upper panel of Fig. 3), the bonding region $[-8, -3 \text{ eV}]$ is formed by Mn- e_g and C- p hybridized states with a strong σ -type overlap characteristic of the octahedral arrangement. Next, the nonbonding part is dominated by the Mn- t_{2g} manifold from -3 to $+1 \text{ eV}$. In the remaining higher-energy window, the Mn- e_g and C- p hybridization forms the antibonding counterpart. The RS phase has clearly a metallic behavior, and the small exchange splitting indicates a low-spin configuration; with a magnetic moment value of $\sim 1.15 \mu_B$ arising primarily from the Mn- t_{2g} states.

In the zinc-blende structure, the crystal-field splitting is obviously inverted due to the tetrahedral environment, such that the Mn- t_{2g} orbitals form the bonding manifold. As displayed in Fig. 3 (lower panel), the bonding region $[-6, -3 \text{ eV}]$ contains hybridized Mn- t_{2g} and C- p states. The nonbonding region is dominated by two Mn- e_g bands (one occupied and one empty), still with a small contribution of Mn- t_{2g} . Above $+1.5 \text{ eV}$, the antibonding region contains essentially C- p and Mn- t_{2g} hybrid states. The large separation between bonding and antibonding parts of the Mn- t_{2g} manifold indicates the high strength of the Mn-C bond. More importantly, zinc-blende MnC is insulating in the majority-spin channel with an energy gap of about 1.2 eV , while being metallic in the minority-spin one. This yields a half-metallic ferromagnet with $1 \mu_B$ magnetic moment (from the occupied Mn- e_g band), consistent with previous predictions [26–28].

Although SCAN predicts the correct ZB ground state, its electronic PDOS spectra are very similar to those of PBEsol

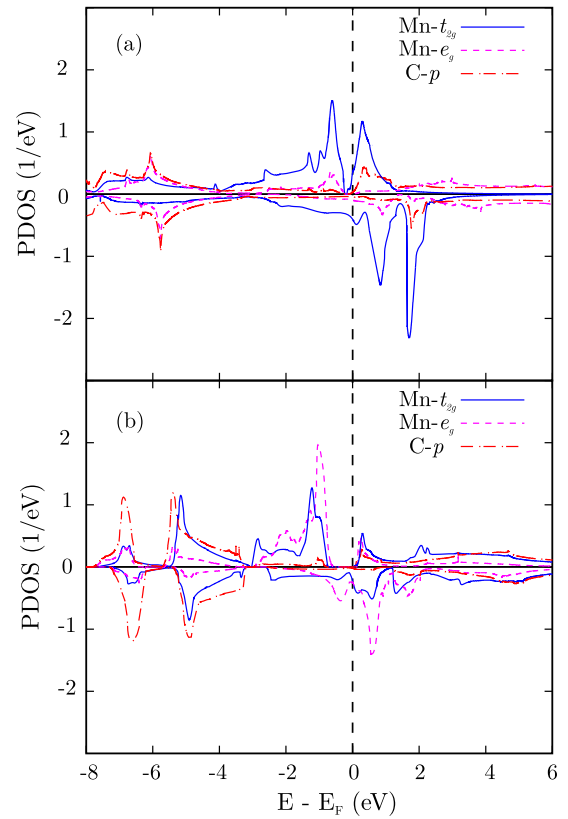


FIG. 4. Atom- and spin-resolved densities of states (PDOS) of MnC in RS-type (a) and ZB-type (b) structures, as arising from the SCAN spin-polarized FM calculations.

(see Fig. 4). In fact, it has been already pointed out that meta-GGAs (including SCAN) do not really improve over GGA for electronic and magnetic properties (band gaps, magnetic moments) [44,46,48].

Within SCAN framework, MnC is also predicted as a ferromagnetic metal in rocksalt structure and a ferromagnetic half metal in zinc-blende one. The whole distribution of the bonding, nonbonding, and antibonding regions is almost identical to PBEsol. The only noticeable difference is that the Fermi level is slightly pushed upward at the vicinity of a nonvanishing DOS, placing the compound near a fully metallic state. Such sensitivity to the lattice constant (here, SCAN: $4.28 \text{ \AA}$ versus PBEsol: $4.22 \text{ \AA}$) has been mentioned previously, where a small increase drives zinc-blende MnC from half-metallic to metallic state [26,27].

B. Hybrid PBE0r and HSE06

To assess the effect of a partial inclusion of the nonlocal HF exchange, we used PBE0r and HSE06 hybrid functionals with two different fractions, 10 and 30%. In each crystalline phase, both fractions yield typically similar trends in the electronic PDOS (bonding, nonbonding, and antibonding regions). The only difference is the stronger exchange splitting with the larger fraction, producing larger magnetic moments. The electronic PDOS obtained from PBE0r and HSE06 are displayed in Fig. 5 and Fig. 6, respectively. As a first result, the two functionals lead to a metallic MnC in both RS and ZB structures.

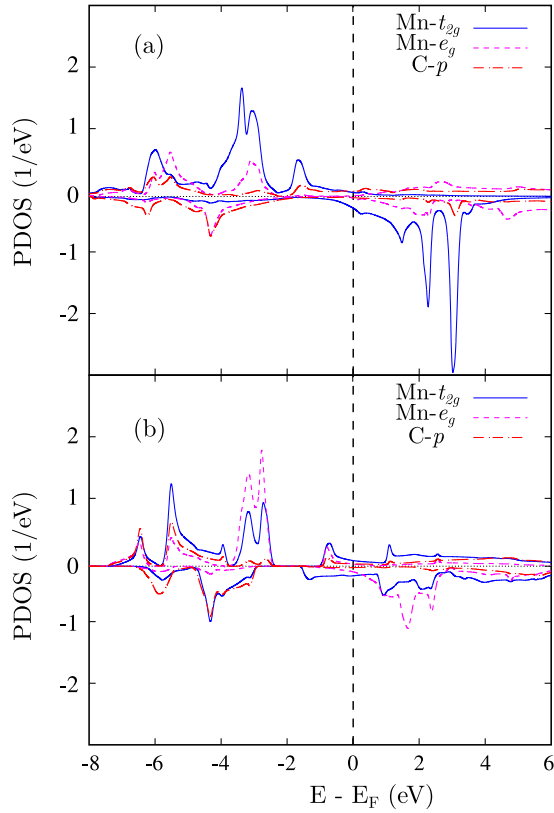


FIG. 5. Atom- and spin-resolved densities of states (PDOS) of MnC in RS-type (a) and ZB-type (b) structures, as arising from the PBE0r, with bond exchange (offsite= T), spin-polarized FM calculations.

In the rocksalt phase, the inclusion of exact exchange substantially enhances the spin splitting of the Mn-3d states, especially for the nonbonding Mn- t_{2g} ones. In PBE0r, the corresponding shift is more pronounced, so that the majority (minority) spin states are almost filled (empty). This drives the Mn- t_{2g} manifold (threefold degenerate) to a quasi-high-spin configuration, whereby the value of the magnetic moment $\simeq 3 \mu_B$ (see Table II). In HSE06, a similar situation is found but with a slightly less important splitting.

In the zinc-blende structure, the same description holds for the two hybrid functionals. The Mn- e_g manifold (twofold degenerate) experiences the largest exchange splitting, driving it toward a high-spin configuration, consistently with the computed magnetic moments. However, in contrast to the semilocal functionals, both hybrid PBE0r and HSE06 predict a fully metallic ZB-MnC at theoretical equilibrium. The disappearance of the half metallicity is primarily due to lattice expansion, since both hybrid functionals yield larger equilibrium volumes (see Table II), in complete agreement with GGA predictions.

To confirm this important result, additional PBE0r and HSE06 calculations have been carried out for ZB-MnC, at the reduced lattice constant arising from PBEsol and SCAN. The corresponding results, shown in Fig. 7, indicate clearly that the majority-spin gap reappears and the half metallicity is restored. The only noticed difference compared to semilocal (PBEsol and SCAN) functionals is the larger majority-spin

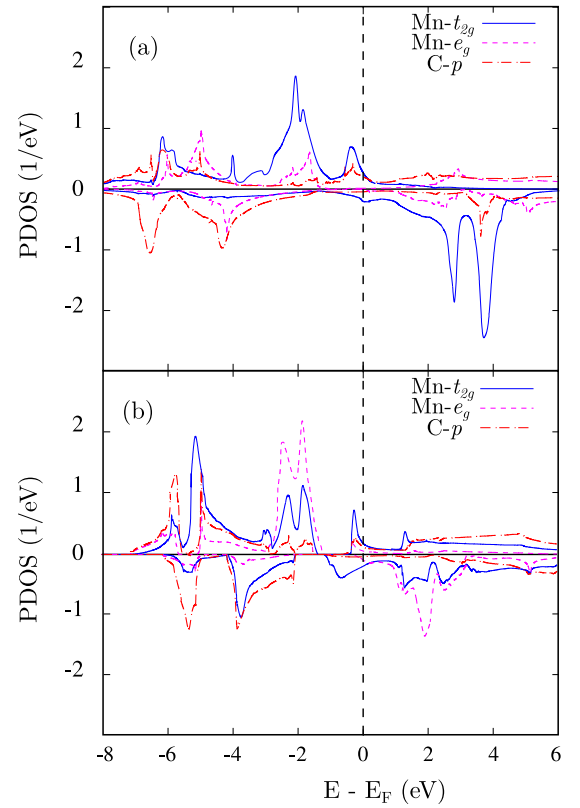


FIG. 6. Atom- and spin-resolved densities of states (PDOS) of MnC in RS-type (a) and ZB-type (b) structures, as arising from the HSE06 spin-polarized FM calculations.

band gap, which is the main effect of the nonlocal exact exchange. Thus, semilocal as well as hybrid functionals agree that ZB-MnC is a half metal at reduced volumes ($\leq 4.3 \text{ \AA}$) and becomes metallic under expansion. Consequently, the compound is expected to behave as a ferromagnetic metal at the experimental lattice constant ($\sim 4.4 \text{ \AA}$).

C. Mean-field DFT + U + V

The DFT + U + V framework offers a complementary picture by explicitly introducing on-site U and intersite V Coulomb interactions. These parameters are computed self-consistently using the linear response DFPT method, and the obtained values at theoretical equilibrium are shown in Table III. For sake of completeness, we also provide the computed values at the PBEsol equilibrium, and at the zinc-blende experimental lattice constant ($4.43 \text{ \AA}$). While the on-site U remains nearly constant (5.5 – 5.9 eV), the intersite term V decreases with increasing lattice constant, reflecting the reduced overlap between neighboring Mn and C orbitals. These values are smaller than those typically found in strongly correlated transition-metal monoxides (for example, in MnO and NiO the U parameter is larger than 6 eV [104–106]).

The PDOS obtained from DFT + U + V (shown in Fig. 8) reveals several distinctive features. In the rocksalt phase, the Mn- t_{2g} manifold (threefold degenerate) is fully polarized, i.e., in a complete high-spin configuration, giving rise to the largest

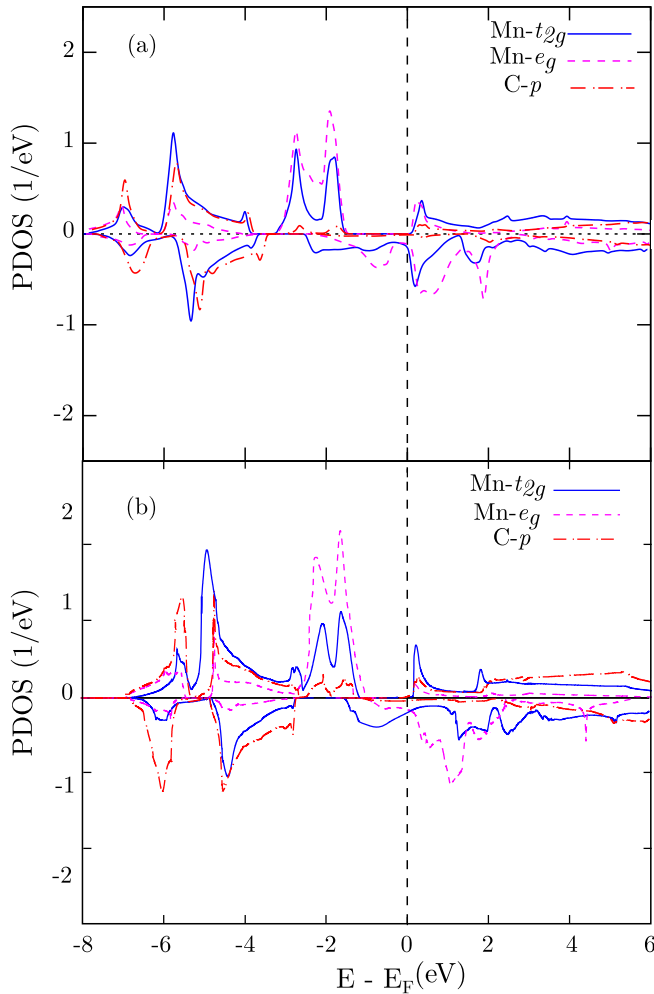


FIG. 7. Atom- and spin resolved densities of states (PDOS) of MnC in ZB-type structure at a reduced volume (lattice constant $a = 4.3\text{\AA}$) within: (a) PBE0r and (b) HSE06 hybrid functionals.

computed magnetic moment value ($M_{\text{fu}} \geq 3 \mu_B$) among all frameworks.

In the zinc-blende phase, the system is in a half-metallic state with a moderate minority-spin gap ($\sim 2.5\text{ eV}$), in contrast to the predictions of hybrid PBE0r and HSE06. The total moment is $3 \mu_B$, where the high-spin Mn- e_g manifold contributes

TABLE III. The calculated values of the on-site U and the inter-site V Hubbard parameters for Mn- $3d$ states, in eV, at DFT + U + V and PBEsol lattice constants, as well as the experimental one. The values are for ferromagnetic solution only, in the rocksalt (RS) and zinc-blende (ZB) structures.

		RS	ZB
a) DFT+ U + V	U	5.60	5.50
	V	0.57	0.70
a) PBEsol	U	5.93	5.85
	V	0.64	0.81
a) Exp.	U		5.53
	V		0.76

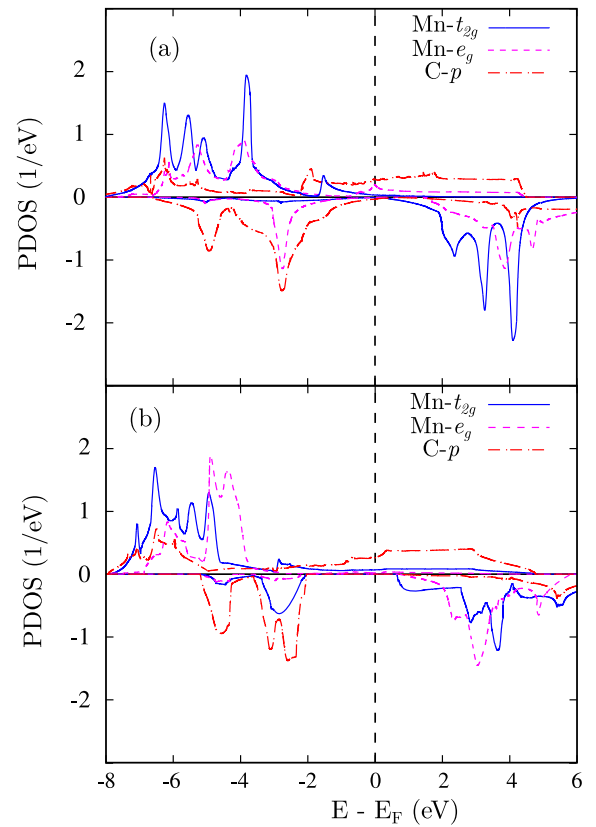


FIG. 8. Atom- and spin-resolved densities of states (PDOS) of MnC in RS-type (a) and ZB-type (b) structures, as arising from the DFT + U + V spin-polarized FM calculations.

with $2 \mu_B$, and the remaining $1 \mu_B$ comes mainly from Mn- t_{2g} states.

Interestingly, while semilocal functionals and DFT + U + V agree on the half metallicity, the band gap resides in opposite spin channels. Curiously, this behavior occurs at a lattice constant ($4.55\text{\AA}$) much larger than the limit ($\leq 4.30\text{\AA}$) predicted by semilocal functionals. Additional DFT + U + V calculations (using the corresponding calculated parameters; see Table III) show that the half metallicity persists at the experimental lattice constant ($4.43\text{\AA}$), and vanishes only under strong compression at the PBEsol volume. This opposite volume trend highlights fundamental differences on how semilocal and hybrid functionals in one side, and Hubbard-corrected ones in the other, treat the MnC half-metallic behavior.

In this context, similar observation has been made for several zinc-blende compounds. For many pnictides, such as Mn(Cr)As(Sb), GGA calculations predicted a half-metallic behavior with a minority-spin gap, disappearing under compression [27]. In the same work, MnC was the only half metal with majority-spin gap.

D. Discussion

Across all theoretical frameworks, the Mn($3d$)–C($2p$) hybridization defines the essential features about the bonding properties and the electronic structure of MnC. Our comprehensive calculations reveal some disagreements on the

TABLE IV. The calculated values of the magnetic moments (in μ_B) carried by Mn atoms in perfect MnC and nonstoichiometric $\text{MnC}_{0.93}$. Mn1 refers to Mn atoms near the vacancy, while Mn2 refers to those situated beyond.

	RS type	ZB type
$\text{Mn}_1\text{C}_{0.93}$	(Mn1)=2.85 (Mn2)=2.65	(Mn1)=2.60 (Mn2)=2.30
Mn_1C_1	2.70	2.35

electronic ground state of ZB-MnC. The failure of some methods reflects the subtle balance of competing mechanisms and the sensitive position of the compound at the boundary between a half metal and a correlated metal. The predictions fall into two distinct categories:

1. Hybrid and semilocal functionals agree that half metallicity appears at small volume and vanishes upon a slight expansion ($\sim 4.30 \text{ \AA}$). At the experimental lattice constant ($\sim 4.43 \text{ \AA}$), accurately provided by PBE0r, MnC is consistently predicted as a metal. The nonlocal exact exchange enhances exchange splitting and yields larger magnetic moments.

2. However, $\text{DFT} + U + V$ favors half metallicity at large volume, but with a different nature. It predicts a robust half-metallic state, persisting at the experimental volume and disappears only under strong compression.

Such theoretical divergence could, in principle, be resolved by experiments, with specific techniques:

- i. direct measurement of the spin polarization at the Fermi level, via spin-resolved photoemission spectroscopy or angle-resolved photoemission;
- ii. high-pressure electrical transport and magnetization measurements could track the volume dependence of the conductivity and magnetic moment.

Therefore, the electronic ground state of MnC remains an exciting question, whose experimental resolution will have significant implications for its practical applications.

Before concluding, we want to briefly assess the effects of carbon vacancies, since the latter are common in transition-metal carbides and can influence bonding, magnetism, and maybe the structural stability [107]. It is expected that the bond-exchange mechanism is locally perturbed by suppressing Mn-C hybridization. Since the exchange splitting (i.e., magnetic stabilization) depends strongly on Mn-C covalency, the p - d hybridization would be reduced around the vacancy, which in turn enhances the localization of Mn- $3d$ states.

So, we have performed additional supercell calculations corresponding to $\text{MnC}_{0.93}$ nonstoichiometric composition (in RS- and ZB-type environments), using the PBE0r hybrid functional. The latter is chosen among the other functionals, because it predicted correctly the ground-state structure and the lattice constant of the perfect compound.

As pointed out, the nearest Mn atoms surrounding the carbon vacancy (noted Mn1) exhibit enhanced exchange splitting, due to the reduced Mn-C hybridization. In contrast, those located beyond (noted Mn 2) display a smaller splitting. This is reflected quantitatively through the computed atomic magnetic moments, as shown in Table IV, especially when

compared to those of perfect MnC. Concerning the electronic character at equilibrium, the nonstoichiometric $\text{MnC}_{0.93}$ behaves as a magnetic metal in both structure types. Finally, the theoretical equilibrium total energies indicate that the compound is more stable in the ZB-type structure than the RS-type one. So, we can conclude that carbon vacancies can alter the magnetic properties and the electronic behavior, but do not have a strong effect on the ground-state structure.

VI. CONCLUSION

A comprehensive first-principles investigation of MnC properties was carried out, using the state-of-the-art of DFT-based methods: PBEsol, SCAN, hybrid functionals (PBE0r and HSE06), and the mean-field $\text{DFT} + U + V$. The main goal was to identify the origin of the experimentally observed zinc-blende structure, and to examine the role of bond exchange in its structural stability as well as electronic behavior.

Our results demonstrate that the stabilization of this experimental structure is uniquely achieved by the SCAN meta-GGA and the PBE0r hybrid functional. This success is attributed to the improved (implicit or explicit) treatment of *bond-directional exchange* interactions in covalent systems. The decisive role of this exchange term is quantitatively proven by its explicit inclusion in PBE0r, which selectively stabilizes the tetrahedral ZB phase by favoring bonding over antibonding states. This shows that an accurate orbital-selective treatment of exchange is crucial for describing the structural chemistry of MnC.

Beyond crystal structure, our investigation reveals a fundamental issue in predicting the electronic ground state. First, at theoretical equilibrium two different behaviors have been found. While semilocal functionals (PBEsol and SCAN) as well as $\text{DFT} + U + V$ predict half metallicity, albeit in opposite spin channel, hybrid functionals (HSE06 and PBE0r) yield a metallic state. However, the volume dependence of the electronic character is curiously different. Semilocal and hybrid functionals are in line, suggesting strongly the stability of the half metallicity at low volume and a disappearance under expansion. On the other hand, the $\text{DFT} + U + V$ approach points towards an opposite volume dependence. This highlights the sensitive position of MnC at the boundary between a correlated metal and a half metal. It establishes the material's electronic state as an open question for both theory and experiment.

Therefore, we conclude that the true ground state of ZB-MnC is best described by a framework that prioritizes bond exchange, such as SCAN or PBE0r. These methods consistently lead to a ferromagnetic metal at ambient synthesis conditions, with a potential transition to a half-metallic state under compression. Taken together, these findings establish MnC as a model system for studying the interplay between covalent bonding and exchange interactions in late $3d$ transition-metal compounds.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request

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